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Preparation and Evaluation of *Cucumeropsis mannii* Naud. Seed Oil Metallic Soaps as Driers in Gloss Paint

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Abstract

The physicochemical properties and fatty acid composition of *Cucumeropsis mannii* (egusi, melon) seed oil was determined. *Cucumeropsis mannii* seed oil was utilized in the preparation of metal soaps of zinc, copper and nickel. The metallic soaps were characterized and applied in gloss paint as driers. The lipid content of *C. mannii* seed was found to be 57.26 %. The iodine value, saponification value, acid value, free fatty acid, peroxide value, specific gravity and refractive index were determined using standard procedures and values were 114.94 gI_2/100g, 220.19 mgKOH/g, 7.09 mgKOH/g, 4.512 %, 20.00 meq/kg, 0.9129 and 1.35 respectively. The seed oil contained palmitic, stearic, oleic, linoleic and linolenic acids, but the most abundant fatty acid is linoleic (64.15 %). Gloss paint was formulated using standard procedure and the metallic soaps were incorporated into the paint as driers. Performance test showed that the metallic soaps acted as a catalyst in the paint matrix, reducing the drying time.

Keywords: *Cucumeropsis mannii*, seed oil, linoleic acid, metallic soaps, gloss paint.

1. Introduction

Cucumeropsis mannii Naud. (melon) is popularly called "*egusi*" in West Africa. This is the true indigenous *egusi* of West Africa [1]. Melon is a cucurbit crop that belongs to the Cucurbitaceae family with fibrous and shallow root system. It is a tendril climber or crawling annual crop, mostly grown as a subsidiary crop interplanted with early maize and yam in some savanna belt of Nigeria [2]. Cucurbit species are among the economically most important vegetable crops and are grown in both temperate and tropical regions [3]. As reported by Jacks *et al.* [4], the seeds has about 50% lipid. Most of their oil is made of non-saturated fatty acids. Conjugated fatty acids among some cucurbitaceae oils make them highly useful as drying oils, that is, they combine readily with oxygen to form elastic, water proof film [5]. Seed oils are important sources of nutritional oils, industrial and pharmaceutical importance [6], and current emphasis on sustainable development has made it imperative to search for industrial raw materials from renewable sources.
Metal carboxylates otherwise called metal soaps have been described as alkaline-earth or heavy-metal long-chain carboxylates [7], which are insoluble in water but soluble in non-aqueous solvents. Their solubility in organic solvents on the other hand, accounts for their use in a wide range of industrial products [8, 9]. Soaps of barium, cadmium, lead, zinc and calcium have found practical application as thermal stabilizers for polyvinyl chloride [10, 11]. Calcium and magnesium soaps are used as corrosion inhibitors in non-polar media; lead, manganese, cobalt and zinc soaps are used in paints to accelerate drying while copper soap

exhibits fungicidal properties [12]. Silver carboxylates are used as the source of silver in thermographic and photothermographic materials [13]. Some have found use in greases, cosmetics, textiles [14]. Metallic soaps have also been used as plasticisers and driers in rubber-based adhesives [15].
The paint industry is probably the highest consumer of metallic soaps. With the phasing out of lead as the primary drier in paints, metallic soaps have become essential components in the manufacture of both emulsion and gloss paints [16]. Soaps of the transition metals act as driers in paint, while those of aluminum, calcium and magnesium function as flattening or leveling agents [17]. Metallic soaps are available commercially and are sold as solids, liquids or powders. They are prepared from fatty acids either by fusion or precipitation processes [18].

A number of seed oils have been characterized but the vast majority have not been explored for the preparation of metal carboxylates despite being the most abundant source of carboxylic (fatty) acids. Melon oil are known to have drying properties, their use in the preparation of the metallic soaps required in the paints could greatly reduce the amount of foreign inputs necessary for the production of paints [19]. There is dearth of information on the industrial utilization of seed oil of melon species. The industrial potential of *Citrullus colocynthis* seed oil as biodiesel feedstock [20]; effect of temperature on the stability of metal soaps of *Trichosanthes cucumerina* seed oil [21] and the oxidative drying of alkyd paints catalyzed by metal complexes [22] have been reported. Hence, the aim of this work is to prepare some metal carboxylates of the *C. mannii* seed oil and evaluate their performance as a dryer in gloss paint.

2. Experimental

2.1 Materials

All chemical used were of analytical grade and were products of BDH Chemicals Ltd, Poole England unless otherwise stated. Melon (*Cucumeropsis mannii*) seeds were purchased from a local market at Nung Udoe-Ibesikpo, Akwa Ibom State, Nigeria. The sample was authenticated by a taxonomist, Dr. (Mrs.) M. E. Bassey of the Department of Botany and Ecological Studies, University of Uyo where a voucher specimen was deposited. The seeds were deshelled, screened, oven dried and ground. The oil was extracted in a Soxhlet apparatus using petroleum ether (40-60 ^{o}C) and solvent removed in vaccuo.

2.2 Physicochemical properties

The physicochemical properties (specific gravity, refractive index, viscosity, moisture content, iodine value, saponification value, acid value, free fatty acid, peroxide value and unsaponifiable matter) of *C. mannii* seed oil were assayed using standard methods [23].

2.3 Fatty acid analysis

The fatty acid composition was determined by GC-Flame Ionization Detection (FID). Methyl esters were obtained by hydrolyzing the triglycerides of the oil with KOH-methanol [23]. GC-FID analysis was performed using a Hewlet Parkard 6890 series GC system equipped with a HP-5 (30 m x 0.22 mm i.d., 5 % dimethylsiloxane; film thickness, 0.25 µm, capillary column with a Flame Ionization Detector. Helium was used as a carrier gas (1mL/min flow rate). Injection and detection temperatures, 250 °C. The column was maintained at an initial temperature of 129 °C for 5 min and then programmed at 2 °C/min to final temperature of 220 °C where it was maintained for 18 min. Fatty acids were identified by retention time relative to an authentic standard. The quantification of fatty acid methyl esters (FAMEs) composition was realized by integration of the FID peak area with the correction factor (internal normalization method).

2.4 Preparation of metallic soap

Metallic soaps of nickel, zinc and copper were prepared by methods adopted by Ekpa and Ibok [15] and Ekpa [24]. The melon seed oil (50 g) was heated to 90-95 ^{o}C in a 500 ml beaker and 125 ml of 10 M NaOH was added with stirring until the whole mixture emulsified into a thick layer, after which the soap was allowed to cool. The soap was separated from the lye and then washed with cold distilled water to remove excess alkali. A solution of the soap (0.05 M) was prepared in hot water and added with stirring to an aqueous solution of the metal salt (0.15 M).The metallic soaps which precipitated was filtered, washed with distilled water and dried in oven at 40 ^{o}C to constant weight. The BDH analar (99 %) salts used were $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$ and $Ni(NO_3)_2.6H_2O$.

2.5 Analysis of metallic soaps

The properties of the prepared metal soaps were determined using standard procedures. The parameters assessed were percentage yield, pH, colour, texture, moisture content, melting point, apparent bulk density, foaming characteristics, total ash content, metal content and solubility in water, kerosene, acetone and methanol. Metal content in the soaps was determined using Perkin – Elmer Atomic Absorption Spectrophotometer (Lambda 35 model) [23, 25].

2.6 Gloss Paint Production

Formulations for paint production were performed by preliminary trials by varying the amounts of each of the components. The quantity of components in Table 1 gave the best results. The first six components of the mixture (Table 1) were stirred for 30 minutes and after switching off the mixer, other components were added and thoroughly stirred. The paint so obtained was stored. The base or paint paste was poured into four containers and the metallic soap (drier) was introduced in varying amount.

Table 1. Main constituents for making gloss paint.

Components	Values (g)
Titanium dioxide (TiO_2)	40
Alkyd resin	30
White spirit	10
Kerosine	12
Easigel	1
Leuthin	1
Alkyd resin	50
White spirit	40
Alkyl resin	70
Anti-skin	1
Silico resolution	1
White spirit	5

Source: Flick [44]

2.7 Determination of Paint Quality

The quality analysis of the prepared gloss paint was performed using standard procedures. The parameters examined include: Viscosity, density, percent solid or non- volatile content, drying time, dust free (DF), tact free (TF), full hardness (FH), dry for recoating (DFR), Colour Matching Test, adherent to surfaces, resistance to water and heat [17].

3. Results and discussion

3.1 Physicochemical Properties of C. mannii seed oil

The physicochemical characteristics of *C. mannii* are presented in Table 2. The total lipid content was found to be 57.26 %. The result for iodine value, saponification value, acid value, free fatty acid, peroxide value, specific gravity and refractive index were 114.94 gI_2/100 g, 220.19 mgKOH/g, 7.09 mgKOH/g, 4.512 %, 20.00 meq/kg, 0.9129 and 1.35 respectively. The iodine value of *C. manni* oil indicates that the oil is a semi-drying oil. The class of oils whose iodine value is between 100-150 possesses the property of absorbing oxygen on exposure to the atmosphere [26]; they become thicken and remain sticky but do not form a hard dry film. They are used in the production of soap [27, 28]. The saponification value compared favourably with that of palm oil (196–205 mgKOH/g), olive oil (185-196 mgKOH/g), soyabean oil (193 mgKOH/g) and linseed oil (193-195 mgKOH/g) [29]. The high saponification value of *C. mannii* suggests that the oils could be good for soap making and in the manufacture for lather shaving cream [30, 31]. The low peroxide values of the oils indicate that they are less liable to oxidative rancidity at room temperature [32, 33].

Table 2. Physicochemical properties of *C. mannii* seed oil.

TEST	VALUE
Specific gravity	0.9129 ± 0.1
Relative viscosity, Nsm^{-2}	5.89 ± 0.2
Refractive index, 25 °C	1.35 ± 0.1
Moisture content, %	27.30
pH	4.45
Boiling point, ^{o}C	220-320
Colour	Pale yellow
Saponification value, mgKOH/g	220.19 ± 0.4
Acid value, mgKOH/g	7.09 ± 0.2
Free Fatty Acid, %	4.512 ± 0.1
Iodine value, $gI_2/100g$	114.94 ± 0.4
Peroxide value, meq/kg	20.00 ± 0.3
Lipid content, %	57.26

Values are means ± SD of 3 determinations

3.2 Fatty acid composition

The fatty acid profile of *C. mannii* seed oil revealed the presence of five fatty acids: palmitic, stearic, oleic, linoleic, and linolenic acids (Table 3).

Table 3. Fatty acid composition of *C. mannii* seed oil

Fatty acid	Percentage composition (%)
Palmitic	10.57
Stearic	8.333
Oleic	13.65
Linoleic	62.14
Linolenic	5.293

The fatty acid composition of the *C. mannii* oil is comparable with values obtained in previous studies for other melon species [34-38]. Of the five fatty acids, linoleic acid is the most prevalent with the relative abundance of 62.14 % which is reported to be a drying agent in seed oils. The total saturated and unsaturated fatty acids contents of the *C. mannii* seed oil are 18.9 and 81.9%, respectively.

3.3 Analysis of the metal soaps

The properties of metallic soap of Ni, Cu, and Zn are presented in Table 4. The yield, ash content and melting point respectively of Ni soap (42 %, 17.82 %, 114 °C), Cu soap (51%, 14.46%, 110 °C), and Zn soap (53 %, 17.30 %, 120 °C) are comparable with data reported for metal soaps prepared from palm kernel oil [39]. Among the three studied metallic soaps, Zn soap exhibited the highest quality value (yield, 53 %; melting point (120 °C), moisture content (0.45 %), pH range (5.30-6.700) and white powder properties applicable to different shades of paint products. The characteristics of soaps are determined by the amount and composition of the component fatty acids in the starring oil. According to Poulenant *et al*. [40], the melting temperatures of soaps produced from sources other than rubber seed oil are generally higher. Generally, the melting point of the soaps are between 110–120 ^{o}C which makes them suitable for application at these temperatures since high melting point pose solubility and handling problems. The total ash content in the soap (14.46-17.82 %) indicates that there is little or non-combustible organic and inorganic matter in the soap. The moisture content (0.40-0.51 %) shows the presence of a lesser amount of dirt and impurities in the soap. This is very essential for the specification of driers use for these purposes.

Table 4. Properties of the prepared metallic soaps.

Tests	Nickel soap	Copper soap	Zinc soap
pH range	6.72-6.87	4.97-6.81	5.30-6.70
Metal content	6.20	14.21	11.20
Colour	Green	Blue-green	White
Texture	Powder	Powder	Powder
Moisture content (%)	0.51	0.40	0.45
Melting point (^oC)	114	110	120
Apparent bulk density	0.81	0.77	0.77
Total ash content (%)	17.82	14.46	17.30
Yield (%)	42	51	53
Foaming characteristic	Does not foam in H_2O	Does not foam in H_2O	Does not foam in H_2O
Solubility	Insoluble in H_2O and soluble in kerosene and acetone	Insoluble in H_2O and soluble in kerosene, acetone and methanol.	Insoluble in H_2O and soluble in kerosene, acetone and methanol

3.4 Gloss paint production

The gloss paint formulations were obtained by varying the quantity of metal soaps incorporated into the paint matrix which yielded Sample A, B, C and control sample (Table 5). For optimum result, the metallic soaps were combined to serve as active and auxiliary driers. Cu soap (active or surface driers) combined with Zn soap (auxiliary driers) while Ni soap functioned as stabilizers [41]. Heaton [42] indicated that the amount of driers (active and auxiliary) be calculated before combination to give better results. According to Dosunmu and Ochu [43], melon seed oils possess the potential to exhibit noticeable drying properties required in paint production since they contain an appreciable amount of linoleic (C18:2) acids which is needed for cross-linking during the drying process. Metallic soaps help in accelerating the rate of cross-linking of the double bonds in the unsaturated fatty acids and also increase flexibility of the paint molecules, increasing binding power and better adhesion of the paints on substrates [39].

Table 5. Formulation of gloss paint.

Component	Sample A (g)	Sample B (g)	Sample C (g)	Sample D (g)
Metallic soap (drier)				
Nickel	2.5	3.0	5.0	-
Zinc	3.0	3.5	8.5	-
Copper	3.0	4.0	5.8	-
Titanium dioxide	40.0	40.0	40 .0	40.0
Alkyd resin	30 .0	30.0	30.0	30.0
White spirit	10 .0	10.0	10.0	10.0
Kerosine	12 .0	12.0	12.0	12.0
Easigel	1.0	1.0	1.0	1.0
Leuthin	1.0	1.0	1.0	1.0
$CaCO_3$	8.6	8.5	8.6	8.6
Alkyd resin	50.0	50.0	50.0	50.0
White spirit	40.0	40.0	40.0	40.0
Anti-skimming	1.0	1.0	1.0	1.0
Silico resolution	1.0	1.0	1.0	1.0

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3.5 Determination of paint quality

The drying properties and colour of the paint samples are listed in Table 6. The time required for each of the paint samples to attain full hardness (FH) ranged from 6-7.20 hours. The fatty acid portion of the metallic soap acted as a plasticizer by solvating the polymer molecule to reduce crystalinity; increase flexibility to prevent cracking and peeling off of the paint after application. All the paints had good adherence properties as presented in Table 7. The metallic property in the soap is responsible for the catalytic process leading to the drying of the paints which includes cross-linking of the fatty acid double bonds. Performance and storage properties of the paint are presented in Table 8. None of the paints treated with the metallic soaps showed any signs of chalking, mildew formation, settling or skinning during the period under observations (12 weeks). The quality control parameters of the gloss paint (Table 9) were compared with industrial commercially available gloss paints. The quality of the prepared metallic soap paint samples competed favourably with the selected commercial paints.

Table 6. Drying properties of the paints and their colours.

Sample	Oil used	Colour of paint	Drying Time			
			DF, Min.	TF, Min.	DFR , Min.	FH, Hrs.
A	CMSO	White	12.00	16.00	21.00	7.20
B	CMSO	White	11.00	14.00	19.00	6.40
C	CMSO	White	9.00	11.00	16.00	6.00
D	Control	White	1 day	1 day	2 days	None

DF =Dust Free, TF = Tact Free, DFR = Drying for recoating,
FH = Full hardness, CMSO = *Cucumeropsis mannii* seed oil.

Table 7. Adherence to surfaces of the paint samples.

Sample	Wood	Metal	Wall	Glass
A	VG	EX	EX	G
B	VG	EX	EX	G
C	VG	EX	EX	G
D	P	VP	G	VP

Ex = excellent, VG = very good, G = good, P = poor, VP = very poor

Excellent means film did not show any signs of cracking or peeling after few months. Very good indicates no cracking or peeling off, but required second coating for high gloss. Good indicates film not strongly adhering to surfaces and could peel off when scratched. Poor and very poor implies no adherence.

Table 8. Performance and storage properties of the paints.

Sample	Colour retention	Exterior durability	Water resistance
A	EX	EX	VH
B	EX	EX	VH
C	EX	EX	VH
D	G	VP	VP

Ex = Excellent, VH = very high, G = Good, P = poor, VP = very poor.

Excellent means the film maintained high gloss, no peeling of the painted surface during the period under observation (12 weeks). Very high indicates no wash off or loss of gloss of painted surface. Good indicates painted surface assumed dull colour and showed signs of wash off. Poor and very poor indicate loss of gloss and loss of adhesion.

Table 9. Comparison of quality parameters of the paints with those of industrial paints.

Quality parameters	Paint samples			Industrial paints			
	Sample A	Sample B	Sample C	Saclux	Clover	Kingmos	Royal
Density, g/ml	1.31	1.33	1.38	1.27	0.84	1.12	1.32
Percent solid content, %	66.00	69.00	71.00	72.70	56.10	49.00	74.56
Viscosity, Nsm^{-2}	26.70	27.00	27.50	26.70	24.50	24.20	26.50

Conclusion

Melon seed oils are known to have drying properties; their use in the preparation of the metallic soap required in the paints could greatly reduce the amount of foreign inputs necessary for the production of paints. In this study, nickel, copper and zinc metallic soaps were prepared by precipitation method. The metallic soaps produced by precipitation method are quite effective since good yields of Ni, Cu, and Zn soaps were obtained. The metallic soaps, when introduced into the paint formulation, were found to improve the quality of the gloss paint by imparting such desirable properties in performance such as resistance to water, colour retention, heat, good adhesion to surfaces with reduced drying time. The data obtained represents significant new findings and relevant exploitation of metal soaps from *C. mannii* seed oil in industrial application especially in the paint industry.

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